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# Composition-Explicit Distillation Curves of Diesel Fuel with Glycol Ether and Glycol Ester Oxygenates: Fuel Analysis Metrology to Enable Decreased Particulate Emissions

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We recently introduced several important improvements in the measurement of distillation curves of complex fluids. The modifications to the classical measurement provide for (1) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7) corrosivity assessment of each distillate fraction. We have applied the new method to the measurement of rocket propellant, gasolines, jet fuels, and hydrocarbon crude oils. In this paper we present the application of the technique to representative diesel fuel and mixtures of diesel fuel with some of the more promising oxygenating agents; namely, the glycol ethers and glycol esters: tri(propylene glycol) methyl ether (TPM), dibutyl maleate (DBM), and an 80/20 (vol/vol) mixture of diethylene glycol methyl ether (DGME) + 1,2-dimethoxyethane (DME) a mixture often referred to as Cetaner. We present not only the distillation curves but also a chemical characterization of each fraction, and discuss the contrasts between the various mixtures. The measurements are significant as an environmental design tool for decreased particulate emissions.

## Introduction

One of the most important and informative parameters that is measured for complex fluid mixtures is the distillation curve (1, 2). It has been possible in recent years to relate the distillation curve to many environmental parameters of complex liquid fuels. For gasoline and diesel engines, these parameters include engine starting ability, vehicle drivability, fuel system icing and vapor lock, fuel injection schedule, and fuel autoignition, etc. It is also possible to correlate the distillation curve of diesel fuels with exhaust emissions such as carbon monoxide, particulates, nitrogen oxides, and unburned hydrocarbons. Beyond rough prediction of emissions, it has also been possible to relate the mutagenic effects of diesel fuel emissions to the distillation curve as well (3–5).

This implies that one can use the distillation curve in the design of fuels that have a decreased genotoxicity. It will not be possible to apply new reformulated diesel fuels in new engines without the distillation curve as an input.

Diesel engine designers have increasingly come under pressure to improve environmental performance. Although very efficient, diesel engines have had difficulties achieving desirable emission targets, especially for soot and NO<sub>x</sub> formation. Improvements have been made in the design of fuel systems, combustion chambers, and engine control, and reformulation of diesel fuel has been given renewed attention (6–11). This has focused on two aspects of the fuel: (1) reformulation to lower the sulfur specification, and (2) reformulation to incorporate oxygenates into the fuel (12–16).

The first aspect (the sulfur specification) is more related to issues of SO<sub>x</sub> related acid precipitation rather than to soot and NO<sub>x</sub> formation (17). Indeed, this goal has substantially been met as of 2007, with the introduction of ultra low sulfur diesel fuels that meet the target 15 ppm (mass/mass) specification. The second goal is still the subject of research.

Reformulation of diesel fuel to include oxygenates has been an effective way to reduce soot and NO<sub>x</sub> emissions, to enhance the ability to recirculate exhaust gases, to reduce in-cylinder radiative heat transfer (and improve efficiency), and may enable the application of more sophisticated after treatment technologies. It might be possible to produce completely smoke-free operation of a diesel engine by the incorporation of 38% (mass/mass) of oxygen into the fuel (18). Since reformulation is usually done by mixing oxygenates directly into the diesel fuel, such reformulations are applicable to biodiesel as well. Four major classes of chemical additives have been considered for diesel oxygenates: alcohols, ethers, glycol ethers, and glycol esters (19–33). For a variety of reasons, the glycol ethers and glycol esters are the most promising (22, 34). These compounds have been extensively studied for their solvent properties, so a great deal is known about their behavior (22, 35). The most promising oxygenate additives that have been identified for diesel fuel are tri(propylene glycol) methyl ether (TPM, CAS No. 20324-33-8), dibutyl maleate (DBM, CAS No. 105-76-0), and a mixture of diethylene glycol methyl ether (DGME, 2-methoxyethyl ether CAS No. 111-96-6) + 1,2-dimethoxyethane (DME, monoglyme, dimethyl glycol, ethylene glycol dimethyl ether, dimethyl cellosolve CAS No. 110-71-4). When the mixture of DGME + DME is prepared in a ratio of 80/20 (vol/vol) DGME/DME, the resulting mixture is often referred to as Cetaner. We note that the most common industrial fluid supplied as TPM is actually a mixture of the 2,2,1- and the 2,2,2- isomers, with the 2,2,2- isomer predominating. In the mixture, the methylated group can “float” between the number one or two carbons of each ethoxylated unit. Many of these glycol ethers and esters have been very well studied as industrial solvents. Some representative properties of these fluids are provided in Table S1 of the Supporting Information.

In earlier work, we described a method and apparatus for an advanced distillation curve measurement that is especially applicable to the characterization of fuels. This method is a significant improvement over current approaches, featuring (1) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6)

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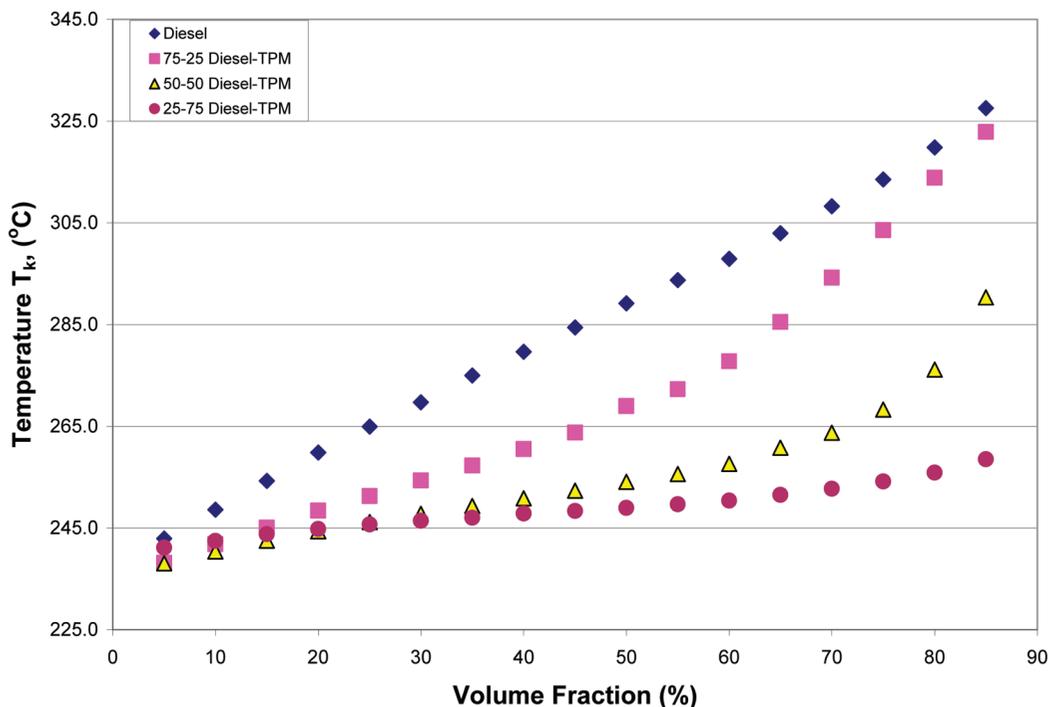


FIGURE 1. Distillation curves, presented in  $T_k$ , for diesel fuel and three mixtures of diesel fuel with tri(propylene glycol) methyl ether (TPM). The uncertainties of the measurements are discussed in the text.

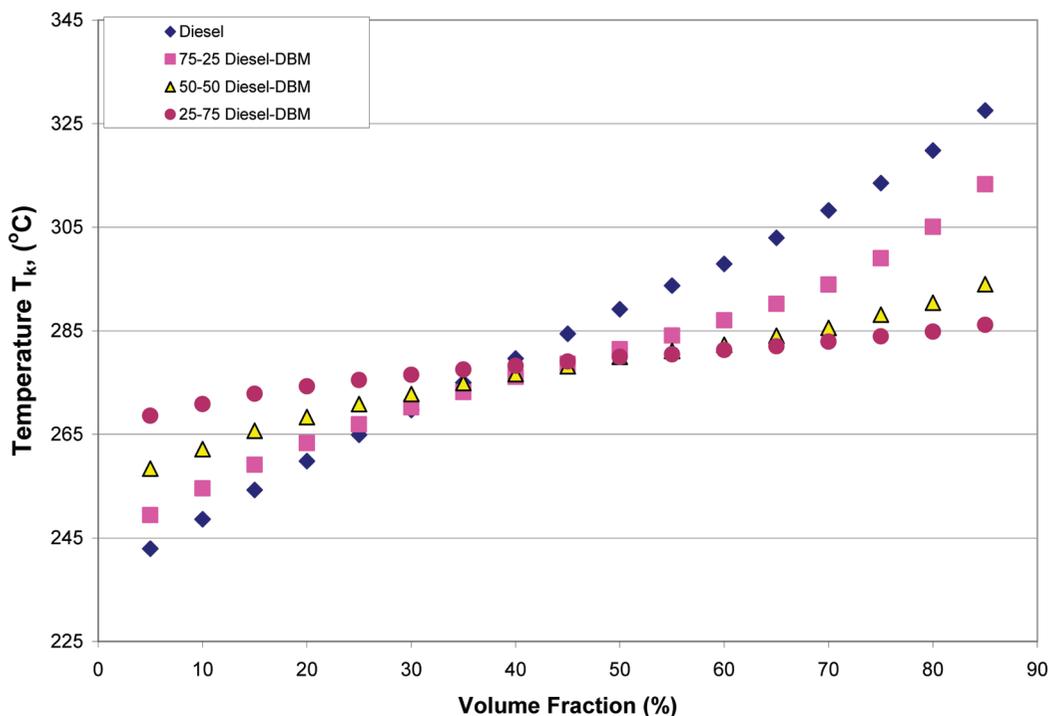


FIGURE 2. Distillation curves, presented in  $T_k$ , for diesel fuel and three mixtures of diesel fuel with dibutyl maleate (DBM). The uncertainties of the measurements are discussed in the text.

trace chemical analysis of each distillate fraction, and (7) corrosivity assessment of each distillate fraction (36–43). For diesel fuels, as with any fuel, the distillation curve is one of the main operational and design parameters used to ensure good engine performance and pollutant minimization. Moreover, it was recently cited as one of the properties most needed in the development of diesel fuel surrogates for advanced fuel research (44). We have applied this metrology to gasolines, aviation fuels, and rocket propellants (36–43, 45–55). In the work reported here, we have applied the advanced distillation curve technique to diesel fuel and

oxygenates of diesel fuel made with glycol ether and ester fluids. This new metrology and the resulting measurements will be important in the application and adoption of oxygenated diesel fuels.

Indeed, a major advantage of distillation curves that are true thermodynamic state points is that models can be developed with accurate equations of state, rather than the simple fit models possible now (56, 57). In this respect, the measures of environmental favorability (low genotoxicity and low particulates) and engine performance parameters, and the trade-offs these parameters entail, can be evaluated

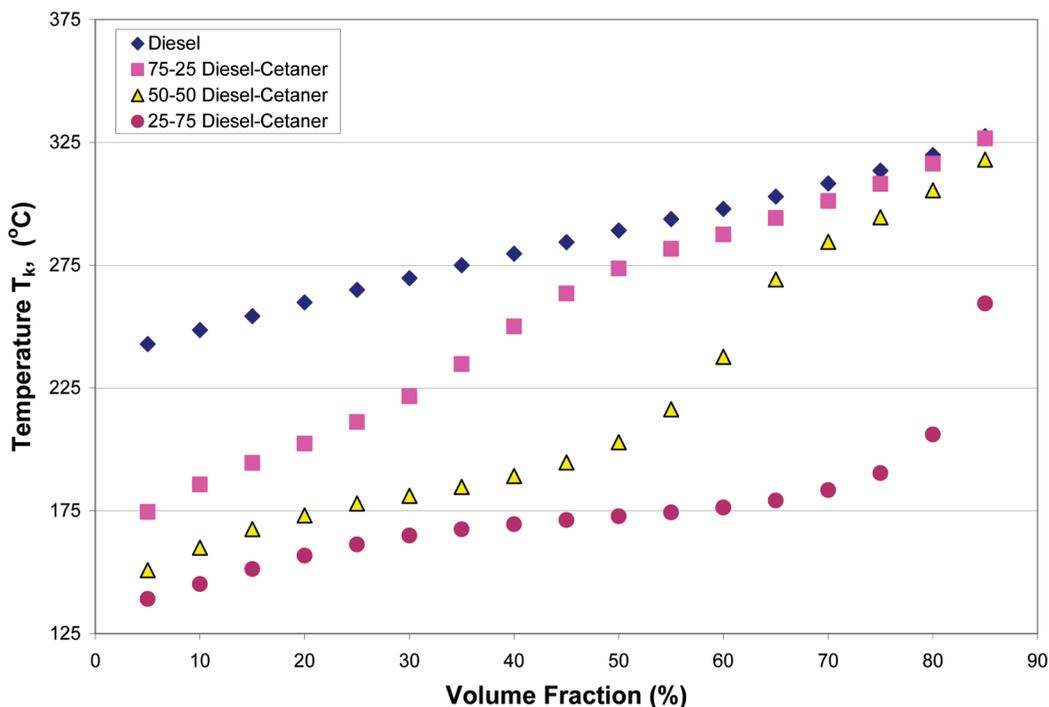


FIGURE 3. Distillation curves, presented in  $T_k$ , for diesel fuel and three mixtures of diesel fuel with the mixture called Cetaner (diethylene glycol methyl ether, DGME, and 1,2-dimethoxyethane, DME, in a volume ratio of 80/20). The uncertainties of the measurements are discussed in the text.

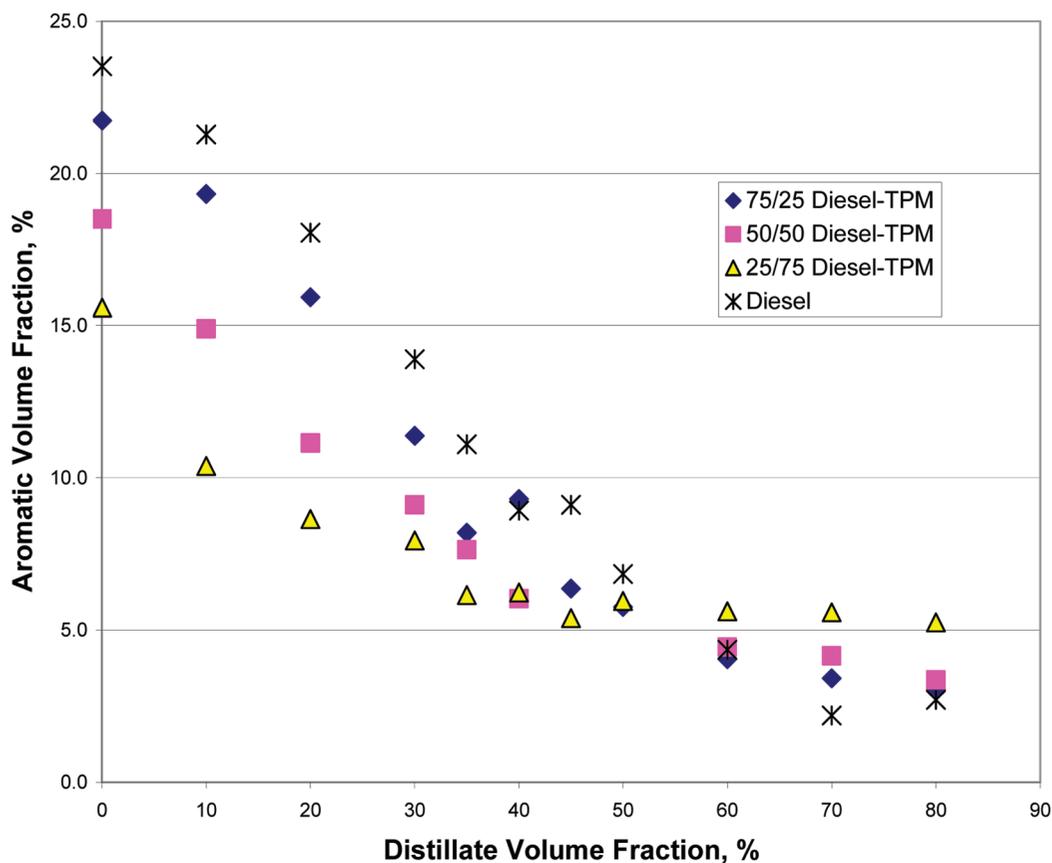


FIGURE 4. Plot of the aromatic content of diesel fuel and three mixtures of diesel fuel with TPM, as determined with ASTM D2789 method.

from the advanced distillation curve, especially the later region from 50 to 90% distillate. For example, lower temperatures in this curve area correlate with lower genotoxicity, but this could be limited by the onset of unfavorable ignition delay in new engines (5). Thus, the tradeoff can be represented

and designed for with reference to the advanced distillation curve result. This can be as simple as matching the oxygenated curve as closely as possible with the operating curve for the particular engine, or as complex as a comparison with an equation of state, directly incorporated into a process

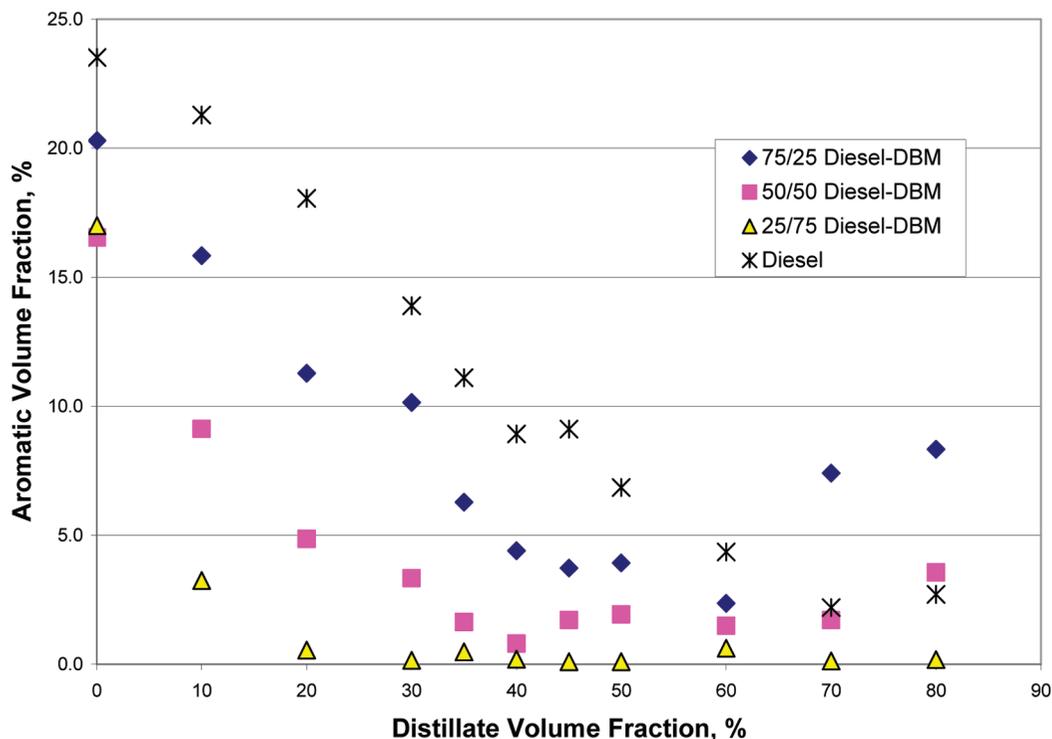


FIGURE 5. Plot of the aromatic content of diesel fuel and three mixtures of diesel fuel with DBM, as determined with ASTM D2789 method.

simulator program. Likewise, particulate soot formation is negatively correlated with temperature and oxygenate concentration (58). The tradeoffs can be analyzed and be made in the same way as discussed above. Thus, the advanced distillation curve unites operability parameters (such as ignition delay) and environmental impact parameters (genotoxicity and particulate emission) in a single design tool.

### Experimental Section

The diesel fuel used in this work was obtained from a commercial source and was stored at 7 °C to preserve any volatile components. No phase separation was observed. The fuel was a winter grade, low wax, ultra low sulfur diesel fuel that incorporated a red dye (specifying off-road use), and was refined locally from petroleum of the Denver-Julesburg field. This fluid was used without any purification or modification. The composition was studied with a gas chromatographic method (30 m capillary column of 5% phenyl–95%–dimethyl polysiloxane having a thickness of 1 μm, temperature program from 90 to 275 °C, 9 °C per minute) using flame ionization detection and mass spectrometric detection.

The tri(propylene glycol) methyl ether (TPM, the 2,2,2-isomer), dibutyl maleate (DBM), diethylene glycol methyl ether (DGME), and 1,2-dimethoxyethane (DME) were obtained from commercial sources as reagent grade fluids. The purities of these fluids were verified with a chromatographic method similar to that specified above for the diesel fuel. The purity of TPM, DGME, and DME was found to be approximately 99.5% (mass/mass), while the DBM was found to have approximately 2% of the dibutyl fumarate isomer. This isomer is so closely related to DBM, however, that it is not considered a significant factor in this work. A moisture analysis was done with Karl Fisher Coulombic titrimetry. No more than 10 ppm (mass/mass) water was found. Care was taken in the handling of these fluids. Specifically, DBM is an irritant, while DGME and DME may impair fertility and can form explosive peroxides. We stress that in this work we used reagent grade fluids; the fluids that are typically encountered

in industrial applications are often mixtures of isomers, with one isomer predominating. Moreover, the industrial fluids often have higher water content than the reagents used here. Since the ultimate goal of our work is the development of equations of state to facilitate sound environmental designs, it was essential that we proceed with pure components.

The *n*-hexane used as a solvent in this work was obtained from a commercial supplier, and was analyzed by gas chromatography. The purity was found to be approximately 99.9 mass percent, and the fluid was used without further purification.

The mixtures of the diesel fuel with the oxygenating fluids were prepared volumetrically in mixing cylinders that had an uncertainty of 0.1 mL. For each oxygenate blend, mixtures with 75, 50, and 25% diesel fuel (vol/vol) were prepared. The differing physical properties of the hydrocarbon species in diesel fuel and the various oxygenates were apparent during the preparation of the mixtures. The hydrocarbon mixture in diesel fuel typically has a density of 0.75–0.85 g/mL, while the density of the oxygenate compounds is much higher, approximately 0.96 g/mL. To characterize these mixtures, some representative thermophysical properties were measured. These are compiled in Table S2 (Supporting Information) in which the measured density, refractive index, and absolute viscosity at 20, 25, and 30 °C at atmospheric pressure (82.5 kPa) are provided.

The method and apparatus for the distillation curve measurement has been reviewed in refs 36–43 so additional description will not be provided. Since the measurements of the distillation curves were performed at ambient atmospheric pressure (measured with an electronic barometer), temperature readings were adjusted for what should be obtained at standard atmospheric pressure with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000109 (59). The actual measured temperatures are easily recovered from the Sydney Young equation at each measured pressure.

## Results and Discussion

**Initial Boiling Temperatures.** During the initial heating of each sample in the distillation flask, the behavior of the fluid was observed. Direct observation through the flask window or through the illuminated bore scope typically allowed measurement of the onset of boiling for each of the mixtures. During the early stages of a measurement the first bubbles will appear intermittently, and this action will quell if the stirrer is stopped momentarily. Sustained vapor bubbling is then observed. Finally, the temperature at which vapor is first observed to rise into the distillation head is observed. This is termed the vapor rise temperature. These observations are important because they are the initial boiling temperatures (IBT) of each fluid. Moreover, these temperatures can be modeled theoretically, for example, with an equation of state.

The dark red dye present in the diesel fuel sample that we used prevented a measurement of the onset of bubbling and the sustained bubbling temperatures in the pure diesel fuel and in two of the mixtures containing 75% diesel fuel. Fortunately, the vapor rising temperature could still be determined. These measurements, presented as averages of three separate determinations, are provided in Table S3 (Supporting Information). As with all observations of these initial temperatures, there is an element of subjectivity. For example, it is often difficult to distinguish between the onset of initial bubbling and the entrainment of air bubbles by the action of the stirrer. Since we have several replicate observations for each sample, it is possible to assign an uncertainty to these temperatures (despite the subjectivity in the observation) since these observations are made for each distillation curve measurement. The uncertainty in the onset and sustained bubbling temperatures is approximately 2 °C for the mixtures in which this could be observed. The uncertainty in the vapor rise temperature is actually much lower, at approximately 0.2 °C. As we have noted for all other fluids measured with the advanced approach, the IBT values we have presented are very different from those that would be obtained with the classical method, in which the first drop of distillate to arrive at the receiver triggers the reading of the IBT. We have shown those values measured with the classical approach to be between 7 and 13 °C in systematic error.

Examination of the initial behavior temperatures reveals the expected trend when considering the oxygenate mixtures. The oxygenating fluid with the highest relative molecular mass (RMM) and boiling temperature, DBM, produces mixtures with higher initial boiling temperatures than those of diesel fuel. The Cetaner mixture, which has a relatively low RMM and boiling temperature, produces mixtures with diesel fuel in which the onset of boiling is significantly below that of diesel fuel. The mixtures with TPM show an intermediate behavior, very similar to that of diesel fuel itself.

**Distillation Curves.** Representative distillation curve data for the samples of diesel fuel and mixtures of diesel fuel with oxygenating fluids, presented in both  $T_k$  (measured directly in the fluid) and  $T_h$  (measured in the distillation head), are provided in Table S4 (Supporting Information). The  $T_k$  data are true thermodynamic state points while, the  $T_h$  data allow comparison with earlier measurements. In this table, the estimated uncertainty in the temperatures is 0.1 °C. Note that the experimental uncertainty of  $T_k$  is always somewhat lower than that of  $T_h$ , but as a conservative position, we use the higher uncertainty value for both temperatures. The uncertainty in the volume measurement that is used to obtain the distillate volume fraction is 0.05 mL in each case. The uncertainty in the pressure measurement (assessed by logging a pressure measurement every 15 s for the duration of a typical distillation) is 0.001 kPa. The relatively low uncertainties in the measured quantities facilitate modeling the results,

for example with an equation of state. The same data are provided graphically in Figures 1–3. The shapes of all of the curves are of the subtle sigmoid type that one would expect for a highly complex fluid with many components, distributed over a large range of relative molecular mass.

For the mixtures of diesel fuel with TPM, shown in Figure 1, we note that as the quantity of TPM increases in the mixture, the distillation curve drops to lower temperatures as the distillation proceeds. In the early distillate fractions, this behavior is rather subtle, and is in fact consistent with our observation of the onset behaviors summarized in Table S3 (Supporting Information). As the distillations progress, the temperatures become more divergent, especially in the middle of the curves. In the latter stages of the distillations (for the 75/25 and 50/50 diesel/TPM mixtures), the curves for the mixtures again begin to tend toward the diesel fuel curves, indicative of the loss of oxygenate. In the 25/75 mixture, the behavior is somewhat different. This mixture is clearly dominated by the large presence of TPM, and the curve is very flat, similar to that of a pure fluid. We have seen in previous work that the difference between  $T_k$  and  $T_h$  is a useful indicator of this behavior. Indeed, in the case of azeotropes and pure fluids,  $T_k$  and  $T_h$  converge and are identical within experimental uncertainty. In the case of each of these mixtures, we can examine the average difference of  $T_k$  and  $T_h$ : diesel fuel, 26.4 °C; 75/25, 15.1 °C; 50/50, 10.7 °C; 25/75, 4.2 °C. This temperature behavior is consistent with that of a mixture that is dominated by a particular component, rather than the onset of an azeotrope. The temperature difference observed for the 25/75 mixture is much less than that of the other mixtures, consistent with the very gentle slope apparent for this mixture in Figure 1.

The distillation curves of the diesel fuel mixtures with DBM are strikingly different from those with TPM, as shown in Figure 2. Here, the mixtures are progressively less volatile than diesel fuel, and the distillation curves begin at higher temperatures. Moreover, as with the mixtures with TPM, the slope becomes less pronounced as the quantity of DBM increases. For the 25/75 mixture, we see the mixture tending toward pure fluid behavior. We can again examine the average difference of  $T_k$  and  $T_h$ : diesel fuel, 26.4 °C; 75/25, 27.8 °C; 50/50, 14.6 °C; 25/75, 10.6 °C. We observe a crossover point in the curves (at distillate volume fraction of approximately 40%) at which the volatility trends of the curves reverse. At this point (the crossover) and beyond, the distillation temperatures of the mixtures containing a higher volume fraction of diesel fuel exceed those of mixtures containing a higher volume fraction of DBM.

The distillation curves for the diesel fuel mixtures with Cetaner are typical of curves for fluids that have very large differences in boiling temperatures among the components. The curves for the mixtures are initially much lower in temperature than that of diesel fuel, but as the lighter components distill out, the curves approach that of the diesel fuel. While we observe the same trend in the difference between  $T_k$  and  $T_h$  (that of, on average, tending to converge as the quantity of Cetaner increases), we also note that as the Cetaner is depleted at the later stage of the distillations, the temperatures begin to diverge. This is especially apparent for the 25/75 mixture.

**Distillate Stratification.** An unusual distillate behavior was noted in the course of these measurements on diesel fuel oxygenated with glycol ether and ester fluids. It was noted that for many of the mixtures we measured, the collected distillate stratified into discernible layers. This kind of behavior has not been noted previously in our measurements on simple hydrocarbon mixtures, gasoline and gasoline oxygenates, rocket propellant, or aviation fuels (including

alternative aviation fuels made from petroleum, natural gas or coal). We have summarized this behavior in Tables S5 and S6.

**Hydrocarbon Type Classification.** The distillate fractions of the diesel fuel and the mixtures of diesel fuel with the glycol ether and glycol ester oxygenates were examined for hydrocarbon types by use of a mass spectrometric classification method summarized in ASTM Method D-2789 (60). In this method, one uses mass spectrometry (or gas chromatography–mass spectrometry) to characterize hydrocarbon samples into six types. The six types or families are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (arenes or aromatics), indanes and tetralins (grouped as one classification), and naphthalenes. Although the method is specified only for application to low olefinic gasolines, and it has significant limitations, it is of practical relevance to many complex fluid analyses, and is often applied to gas turbine fuels, rocket propellants, and missile fuels. The uncertainty of this method and the potential pitfalls were treated earlier (40, 41). As discussed above, the solutions were prepared from 7  $\mu\text{L}$  samples of distillate fraction that were dissolved in a known mass of solvent (*n*-hexane). This solvent was chosen because it causes no interference with the sample constituents. For the hydrocarbon type analysis of the distillate fraction samples, 1  $\mu\text{L}$  injections of these solutions were made into the GC–MS. Because of this consistent injection volume, no corrections were needed for sample volume.

The results of these hydrocarbon type analyses for mixtures with TPM and DBM are presented in Tables S5a–g (Supporting Information). Unfortunately, the mixtures with Cetaner could not be analyzed with this approach because the constituents of Cetaner cause an unfavorable interference with the aromatic *m/z* peak suite. All of the distillate fractions presented in the table were measured in the same way (*m/z* range from 15 to 550 relative molecular mass units gathered in scanning mode, each spectrum corrected by subtracting trace air and water peaks). In general, these tables show that as the concentration of the oxygenate increases, the paraffinic content increases as the distillation proceeds. For mixtures that contain 75% (vol/vol) of oxygenate, the paraffinic content is nearly constant through the distillation. The large number of paraffinic moieties present on the oxygenate molecules ensure this constancy. While this might seem surprising on initial examination, the paraffinic moieties on the oxygenate molecules result in this behavior. The mass spectral analysis measures the paraffin like fragments, regardless of origin from glycol ethers or esters, for example. The same general behavior is observed for all the mixtures in terms of the monocycloparaffins, dicycloparaffins, naphthalenics, and the indanes and tetralins, but at a lower total level.

The variation of the aromatics is particularly interesting however, and the results for these constituents are plotted in Figures 4 and 5. The mutagenicity of a diesel fuel is negatively correlated with the later parts of the distillation curve, and positively correlated with aromatic content of the fuel (5). To a lesser extent, the mutagenicity is also negatively correlated with the naphthalenics in the fuel, as mentioned in the Introduction. Moreover, carbon particulate emission indices correlate with the aromatic content of the later fractions of the distillation curve (61). For diesel fuel, the concentration of aromatic species is seen to decrease as the distillation proceeds. This is the same behavior found with aviation fuels, but with gasolines the opposite was observed. Here, with oxygenated mixtures of diesel fuel, the aromatic concentration is always diluted in the presence of the glycol ethers and esters. We note a slight upturn in Figure 5 in mixtures with DBM, but not with TPM. This is due to an ion formed by DBM at *m/z* = 91; it begins to dominate late in the distillation. The combination of the distillation curves

with this composition information is essential for fuel design since one can simultaneously track the volatility and aromatic content. This also forms the basis for modeling with an equation of state, used directly as an input in engine design with reformulated fuels.

We note also that since the late area (50–90% distillate fraction) of the distillation curve is used in the design of ignition delay and environmental factors such as particulate formation, the composition-explicit data channel is important in that it explicitly relates the quantity of oxygenate remaining with the volatility. This is helpful in uniting two important yet often conflicting sets of parameters: those used for operability and those used to minimize environmental damage. Moreover, we stress that it is not simply the data that are of importance, but the advanced distillation curve metrology, applicable to any complex fluid.

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## Supporting Information Available

Additional experimental data. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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